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Actinide environmental speciation: Source-dependent vs. source-independent species

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Design of the nuclear waste repositories in geological conditions, development of effective remedial actions at radionuclide contaminated sites and evaluation of radioecological impact on the environment requires the molecular-level speciation of radionuclides. In this content the long-lived actinides are of the primary importance since their high radiotoxicity. Recently it has been recognized that environmental behavior of actinides are controlled either by the local geochemical conditions (source independent speciation) or by the source or origin of the contamination (source dependent speciation). In the last case depending on the release scenarios the highly inert “hot-particles” could be formed that demonstrate very high kinetic stability independent on the geochemical conditions. Such “hot-particles” demonstrate very slow solubility and leaching rates. At the same time it has been shown that sorption and redox reactions of actinides at the mineral-water interface also may result in the formation of very low soluble surface precipitates that demonstrate very low leaching rates. To study actinide speciation and to define the conditions that favor the formation of low-soluble inert source dependent and source independent actinide containing particles various spectroscopic (XAFS, XPS, XRF, etc.) and microscopic techniques (radiography, SEM-EDX, HR-TEM) have been applied.

In model experiments under well-defined laboratory conditions the interaction of Pu(IV,V,VI) with minerals (hematite and anatase) at various total concentrations, pH and time intervals have been studied. It was shown that redox transformation of oxidized plutonium, i.e. Pu(V) and Pu(VI), occurs which kinetics is highly dependent on the total concentration of Pu. Redox speciation is done using the kinetics of sorption and leaching, solvent extraction and XAFS. Using Pu LIII XAFS and HR-TEM it was shown that at micromolar concentrations plutonium forms $\text{PuO}_2 \cdot x \cdot n\text{H}_2\text{O}$ nanoparticles with sizes of 1.5-2 nm that are aggregating on the hematite surface. At very low concentration, i.e. $<10^{-14}$ M, it is chemisorbed on the surface of hematite. For anatase only the chemisorbed species are identified at various concentrations of plutonium. The experimental data on plutonium sorption and surface precipitation at various concentrations is interpreted as a competition between chemisorption reaction: $=\text{Xe}-\text{OH} + \text{Pu} \rightarrow =\text{Xe}-\text{O}-\text{Pu} + \text{H}$ (X= Fe or Ti) and surface precipitation: $=\text{Pu}-\text{OH} + \text{Pu} \rightarrow =\text{Pu}-\text{O}-\text{Pu} + \text{H}$. The precipitation of $\text{PuO}_2 \cdot x \cdot n\text{H}_2\text{O}$ nanoparticles result in the formation of highly inert and kinetically stable forms.

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